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(54) **Vitreous bead manufacture**

(57) In a method of manufacturing vitreous beads, a feedstock comprising vitreous particles is fed into a furnace (called a "spherulizing furnace") in which the particles are heated to cause them to spherulize whereafter the spherulized particles are cooled. The feedstock comprises particles of vitreous material which has been subjected to a maximum temperature not exceeding 1400°C in course of its production and such feedstock particles are heated to a temperature above 1400°C in the spherulizing furnace. The use as such feedstock of unrefined or partially refined glass of various compositions such as soda-lime glass and alumino-silicate, alumino-boro-silicate or boro-silicate glass is referred to, as are methods of preparing such a feedstock.

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SPECIFICATION

Vitreous bead manufacture

This invention relates to a method of manufacturing vitreous beads in which a feedstock comprising vitreous particles is fed into a furnace in which the particles are heated to cause them to spherulize whereafter the spherulized particles are cooled. The invention also relates to vitreous particles which can be converted to rounded vitreous beads by heating the feedstock particles in a spherulizing furnace, and to a method of manufacturing such particles.

Vitreous beads fall broadly into two main categories, namely solid beads and hollow beads. Beads in both categories find wide use as fillers for plastics materials for various purposes. Hollow beads are also used as fillers for certain explosives, especially those based on an aqueous emulsion, in order to increase their brisance. Solid beads are also incorporated in paint for the manufacture of reflective signs, for example road signs, and are used for shot- or sand-blasting.

It is well known to manufacture solid glass beads by spherulizing crushed glass cullet, for example originating from waste offcuts from a flat glass manufacturing plant.

Hollow glass beads are usually formed from a feedstock made by pelletising a slip based on a solution of sodium silicate which may have been reacted with some other ingredient such as boric acid and which contains a substance such as urea which will evolve gas when the pellets are vitrified and spherulized in a spherulizing furnace. The vitreous beads formed by such processes necessarily have a rather high alkali metal ion content, which for some purposes is not acceptable. The beads are very susceptible to attack by hydrolysis, in consequence of which the initial adherence between the beads and any plastics materials in which they are used as filler is rapidly weakened and the ageing properties of the filled plastics product are consequently poor. Also, the ageing properties of a filled explosive are poor: the advantage of increased brisance is soon lost, and there will eventually be a reduction in brisance. In order to overcome these disadvantages, such beads may be subjected to an acid leaching treatment to reduce their alkali metal ion content, but such dealkalising treatment adds further to the cost of producing the hollow beads.

Various proposals have been made to produce hollow vitreous beads with compositions which render them less subject to attack by hydrolysis or which confer other special properties on the beads. By way of example United States Patent No 3 365 315 (Beck & O'Brien, assignors to Minnesota Mining and Manufacturing Company [3M]) describes a process of manufacturing hollow glass beads directly from pre-formed amorphous glass particles. Preferably the particles are of a glass which exhibits in the glass melting furnace a viscosity of the order of 10 poises, or an even higher viscosity; and preferably the fusion of the glass batch takes place in an oxidising atmosphere. The amorphous glass particles, unless they contain ab initio, in consequence of the glass formation process, sufficient material which will become gaseous during a reheating step, are subjected to a treatment causing a quantity of such material to become incorporated in the glass. These glass particles are converted to minute spherical glass balloons or bubbles by reheating them, preferably under neutral or reducing conditions, sufficiently to render the glass plastic but preferably not fluid enough to be poured except as an extremely viscous liquid. The recommended temperature for the bubble formation in the reheating step is between 100°C and 300°C lower than the temperature required for the initial glass formation.

The said prior process starting from particles of pre-formed glass is liable to result in bubbles or beads of which at least a significant proportion do not have a form or a clarity good enough to meet the standards sometimes demanded. For example beads having a good standard of sphericity are required for light-reflecting purposes.

The present invention aims to provide a process whereby vitreous beads which are of good quality in regard to form and clarity can be economically produced and which is applicable for forming vitreous beads, including hollow beads, of a wide variety of glass compositions.

According to the present invention, there is provided a method of manufacturing vitreous beads in which a feedstock comprising vitreous particles is fed into a furnace (hereafter called "spherulizing furnace") in which the particles are heated to cause them to spherulize whereafter the spherulized particles are cooled, characterised in that the feedstock comprises particles of vitreous material which has been subjected to a maximum temperature not exceeding 1400°C in course of its production, e.g. in a glass-melting furnace, and in that such feedstock particles are heated to a temperature above 1400°C in the spherulizing furnace.

The invention includes a method of manufacturing vitreous beads, characterised in that vitreous material is withdrawn from a glass production apparatus, e.g. a glass-melting furnace, at a temperature not exceeding 1400°C, such withdrawn material is formed into solid particles, and such particles are spherulized in a spherulizing furnace in which they are heated to a temperature above 1400°C.

Working in accordance with the present invention enables vitreous beads which exhibit a good

form and clarity, to be produced economically. Beads having any of a wide variety of vitreous compositions can be produced by the method. The method can be used for producing solid as well as hollow beads.

Because the vitreous material has been subjected to a maximum temperature not exceeding 1400°C in the melting furnace or other production apparatus, it will necessarily be unrefined or incompletely refined, and it may be incompletely vitrified. The feedstock will therefore will contain a certain amount of dissolved gases and/or gas evolving substances such as sulphates or carbonates. On heating of the particles in the spherulizing furnace, these gases will be driven out of solution or otherwise liberated and will cause expansion of at least some of the particles to form hollow beads.

The vitreous material comprising the feedstock particles can derive from a glass-melting furnace in which the vitreous material is also being made for other purposes, for example for window glazings or hollow-ware, since the material for forming the feedstock particles can simply be drawn off from the glass-melting furnace at an appropriate location before it has reached a temperature of 1400°C, so saving fuel. In the case that the vitreous material is formed in a glass-production apparatus dedicated solely to the formation of material for bead production, the method affords an important economic benefit as compared with the prior process hereinbefore referred to for forming glass bubbles directly from pre-formed glass particles. This benefit is attributable to the lower energy requirements for producing the vitreous particles preparatory to spherulization. Because the maximum temperature in the apparatus is only 1400°C or even less, use can be made of a glass-melting furnace of smaller capacity for a given rate of production so giving savings on capital costs and fuel consumption. Also the relatively low maximum furnace temperature affords the advantage that the refractory material will be eroded less rapidly, so cutting the maintainance costs. That the feedstock must be subjected to higher temperatures in the spherulizing furnace does not negate the fuel economy achieved in the manufacture of the particulate feedstock. The use of such higher temperatures in the spherulizing furnace promotes complete vitrification and refining of the vitreous material of which the resulting beads are formed.

In general the product resulting from operation of a method according to the invention will be a mixture of solid and hollow beads. The method can be performed to yield a preponderance of one or the other kind of beads, as will hereafter be explained. The invention is advantageous for solid bead production as well as for hollow bead production but is of particularly notable benefit in relation to the production of hollow beads. In this specification, the expression "solid beads" denotes beads having a relative density greater than or equal to 1, while the expression "hollow beads" denotes beads having a relative density less than 1. It will be borne in mind that there is a market for solid vitreous beads as well as for hollow beads.

One of the factors influencing the yield of hollow as opposed to solid beads is the way in which gas is liberated in the interior of the feedstock particles during spherulization. In fact gases which are simply dissolved in the feedstock material tend to be driven out of solution at temperatures which are low in relation to the spherulizing temperature of the feedstock particles, and as the particles are heated during spherulization and before the beads are subsequently cooled, some of the bubbles formed in the interior of the feedstock may have time to escape. This of course would reduce the yield of hollow beads. In order to overcome this, and increase the yield of hollow beads, it is especially preferred that said feedstock particles are particles of incompletely vitrified material including chemically bound substance which evolves as gas on heating in the spherulizing furnace. Such substance may for example be a sulphate or a carbonate which has not been fully dissolved in the glass and which evolves SO_3 or CO_2 as the case may be when heated in the spherulizing furnace. Such substances tend to release gases at a temperature which is higher than that at which dissolved gases start to be driven off so the time available for those gases to escape as the beads are being formed is correspondingly reduced, and consequently the yield of hollow beads is increased. It is especially preferred that said feedstock particles include at least 0.25 by weight of chemically bound substance which becomes evolved as gas on heating of the particles in the spherulizing furnace.

The amount of gas evolving substance incorporated in the vitreous material from which the feedstock particles are formed tends to increase accordingly as the vitreous material is withdrawn at a lower temperature from the glass-production apparatus. In preferred embodiments of the invention, the vitreous particles subjected to spherulization are composed of vitreous material which has been subjected to a maximum temperature not exceeding 1370°C in course of its production. In addition to promoting gas evolution during spherulization, the adoption of this feature also promotes fuel economy in view of the lower temperature required.

Another factor influencing the yield of hollow as opposed to solid beads is the granulometry of the vitreous particles feeding to the spherulizing furnace. In general, the smaller the grain size of this feedstock, the more likely the resulting beads are to be solid. This is because bubbles of gas will preferentially form at discontinuities in the structure of the bead forming material, for example at a boundary between vitreous phase and a non-vitreous phase, and the larger the

bead, the more chance there is that there will be such a site well inside the bead, giving the evolved gas less chance to escape. However the composition of the vitreous material of the beads, which is influenced by the maximum temperature to which it has been subjected during its formation is, as already stated, an influential factor. And it has been found that hollow glass beads of very small size, for which there is an important commercial demand, can be produced by a method according to the invention if the particles feeding this spherulizing furnace are of appropriately small size. In some advantageous embodiments of the invention, at least a fraction of the particles feeding the spherulizing furnace are in the size range 20μm to 250μm.

Advantageously, the vitreous feedstock particles are heated to a maximum spherulizing temperature of at least 1500°C in the spherulizing furnace. This promotes gas release within the feedstock and is conducive to the production of clear beads.

Advantageously, the beads, after being cooled, are passed to a settling tank containing water. This is a very simple way of separating solid beads from hollow beads. If desired, the hollow beads can themselves be separated into different density fractions by feeding them to a settling tank containing a liquid medium of appropriate specific gravity.

The invention is applicable for the manufacture of vitreous beads of a wide variety of different compositions. In some preferred embodiments of the invention, said feedstock particles comprise soda-lime glass. Soda-lime glass has the merit of being relatively easy to manufacture and relatively cheap. In other preferred embodiments of the invention, said feedstock particles comprise alumino-silicate, boro-silicate or alumino-boro-silicate glass. Such glasses can impart particularly desirable properties to vitreous beads. Such glasses are usually low in alkali metal ions, so their resistance to hydrolysis is good. Alumino-silicate glasses in particular have high hardness, and alumino-boro-silicate glasses usually have a high Young's modulus. It is especially desirable that hollow vitreous beads should have a good mechanical resistance when they are to be incorporated in a plastics material which is to be injection moulded or extruded, so that they will be able to withstand the pressures involved in such operations. The adoption of this invention gives special advantages in fuel economy when used for the production of low alkali alumino-silicate, boro-silicate or alumino-boro-silicate glass beads since batch materials used for forming those glasses have usually to be heated to at least 1600°C in a glass-melting furnace in order to form an amorphous glass. For forming beads of such a glass by a method in accordance with the invention, the melted batch is withdrawn from the melting furnace at a temperature of 1400°C or even lower. At such temperatures the glass is incompletely vitrified. Vitrification can be completed in the spherulizing furnace. It is important to note that the temperature required for such completion of vitrification in a spherulizing furnace may be lower than that which would be required in a glass-melting furnace.

The invention includes vitreous particles suitable for conversion to glass beads in a spherulizing furnace, characterised in that said particles are composed of vitreous material which has been subjected to a maximum temperature not exceeding 1400°C, and preferably not exceeding 1370°C, in course of its formation, and at least a fraction of such particles are in the size range 20μm to 250μm. Such particles are inexpensive to manufacture, and are very suitable for use as a feedstock in a method as herein defined.

The invention also includes vitreous particles suitable for conversion to glass beads in a spherulizing furnace, characterized in that the said particles are particles of incompletely vitrified material which incorporates at least 0.25% by weight of chemically bound substance which can be converted to gas by heating the particles in a spherulizing furnace to bring about their spherulization. In some embodiments, the said vitreous particles or at least a fraction of them are in the aforesaid size range: 20μm to 250μm. Particles having said amount of gas-evolving substance in chemically bound state are particularly suitable for conversion to hollow glass beads. The chemical bonding delays evolution of gas in the spherulizing furnace, so promoting a high yield of hollow beads. Preferably the vitreous material of said particles includes a said chemically bound gas-evolving substance in an amount such that at least 0.25% by weight of the particles will be evolved as gas on heating of the particles to a temperature of 1550°C.

Advantageously, the vitreous particles are composed of vitreous material which has been subjected to a maximum temperature not exceeding 1370°C in course of its production in a glass-melting furnace. In addition to promoting gas evolution when the feedstock is eventually spherulized, the adoption of this feature also promotes fuel economy during feedstock manufacture, in view of the lower furnace temperature required.

In some some preferred embodiments of the invention, said feedstock particles comprise soda-lime glass, and in other preferred embodiments of the invention, said feedstock particles comprise alumino-silicate, boro-silicate or alumino-boro-silicate glass.

The present invention also extends to a method of manufacturing particles which are spherulizable to form vitreous beads on heating in a spherulizing furnace, which method comprises feeding a vitrifiable batch of appropriate composition to a glass-melting furnace, drawing off melt from the furnace before it has been subjected to a maximum temperature exceeding 1400°C, and solidifying the withdrawn melt and reducing it to particle form. This is a very simple,

convenient and inexpensive way of making those particles. The melt can for example be drawn off from an appropriate temperature zone of a glass-melting furnace from which melt is also drawn off at a high temperature for some other purpose, for example for the manufacture of flat glass or hollow-ware.

In such a method it is preferred that the composition of the batch and the furnace conditions to which the melt is subjected before withdrawal are such that the resulting particles are particles of incompletely vitrified material wherein a substance which evolves gas on heating to a temperature in excess of 700°C is chemically bound in an unvitrified phase. It is especially preferred that the composition of the batch and the heating conditions to which the melt is subjected before withdrawal from the glass-melting furnace are such that the resulting particles include at least 0.25% of a chemically bound substance which can be evolved as gas by heating the particles to a temperature of 1550°C. These features promote favourable evolution of gas when the resulting feedstock is eventually fed to a spherulizing furnace, and the formation of a high yield of hollow beads.

Preferably, the maximum temperature to which the drawn off melt has been subjected in the glass-melting furnace is not greater than 1370°C. This condition is associated with marked economies in fuel production and maintainance costs relating to the glass-melting furnace, and leads to the formation of a product having highly desirable properties for the purposes in view.

Advantageously, the solidified melt is reduced to particles at least a fraction of which are in the size range 20μm to 250μm.

In some preferred embodiments of the invention, said melt is drawn off from the melting zone of the glass-melting furnace. Such melt will be unrefined, and will often contain a certain amount of undissolved batch material which will evolve gas on further heating e.g. in a spherulizing furnace. The amount of undissolved batch material present can readily be controlled by suitable selection of the position in the melting zone from which the melt is drawn off.

It has been found particularly suitable for the purposes of this invention to use a glass-melting furnace which comprises a throat leading between melting and refining ends of the furnace and to draw said melt off from said throat, and this is accordingly preferred.

Advantageously, said melt is allowed to flow through an opening in the sole of the glass-melting furnace whereafter the exiting flow of melt is drenched with water to solidify the melt and shatter it. This is a very simple way of reducing the solidified melt into particulate form. Alternatively, or in addition, ultra-sonic vibrations may be used to shatter the solidified melt. In some circumstances, such granules may be of a suitable size for direct use in a method as hereinbefore defined, but if not, they are suitable for feeding to a suitable crushing device, for example a ball mill, for further reduction in size.

In some preferred embodiments of the invention, the melt which is solidified and reduced to particle form is drawn off from different regions of the glass-melting furnace. The adoption of this feature is of special value when it is desired to produce both solid and hollow beads. Because there are particles which have been drawn from different regions of the furnace, those particles will have different gas evolving properties on heating in a spherulizing furnace. By controlling the relative proportions of such different particles, a measure of control can be exercised over the relative proportions of solid and hollow beads which will be produced when using them as a feedstock in a method according to the invention.

Preferred embodiments of the present invention will now be described by way of Example.

EXAMPLE 1

A conventional vitrifiable batch for the manufacture of boro-silicate glass and containing 4% by weight sodium sulphate is fed to a glass-melting furnace. Melt is drawn off from the furnace in the form of a thread of liquid just before its temperature has reached 1375°C. This thread of liquid is cooled harshly by a jet of cold water so that it solidifies and shatters, and the particles are collected and milled to a mean diameter of 25μm to form a feedstock which is spherulizable to form vitreous beads.

The feedstock particles have the following composition by weight.

SiO_2	74%
Al_2O_3	0.8
CaO	9.4
MgO	0.2
Na_2O	6.4
K_2O	3.3
B_2O_3	5.6
SO_3	0.3

The feedstock is injected into the flame of a burner whose maximum flame temperature is approximately 1550°C for spherulization, and the beads formed are cooled and collected by

means of a cyclone. Inspection shows that the beads are of substantially clear glass and are well formed. The vitreous beads collected are passed to a settling tank containing water for the separation of solid and hollow beads. About 70% by weight of the beads produced were solid with a means diameter of 25μm, the remainder being hollow with a mean diameter of 40μm.

In a variant of this Example, the melt is drawn off from the glass-melting furnace just before its temperature reaches 1350°C. This has the effect of increasing the residual SO_3 content of the feedstock particles to 0.43%, and on spherulization in the same way, the yield of hollow beads is increased to 50%. Again, the result is well-formed beads of substantially clear glass.

EXAMPLE 2

A conventional vitrifiable batch for the manufacture of soda-lime glass and containing 4% by weight sodium sulphate is fed to a glass-melting furnace. Melt is drawn off from the furnace in the form of a thread of liquid just before its temperature has reached 1375°C. The melt is solidified as described in Example 1 and is further reduced to form a feedstock having a mean particle size of 10μm, and the following composition by weight.

SiO_2	72%
Al_2O_3	0.9
CaO	8.7
MgO	3.65
Na_2O	13.8
K_2O	0.25
SO_3	0.7

The feedstock is injected into the flame of a burner whose maximum flame temperature is approximately 1450°C for spherulization, and the beads formed are cooled and collected by means of a cyclone. The beads were well-formed and substantially clear. The vitreous beads collected are passed to a settling tank containing water for the separation of solid and hollow beads. About 70% by weight of the beads produced were solid with a mean diameter of 10μm, the remainder being hollow with a mean diameter of 12μm.

CLAIMS

1. A method of manufacturing vitreous beads in which a feedstock comprising vitreous particles is fed into a furnace (hereafter and in subsequent claims called "spherulizing furnace") in which the particles are heated to cause them to spherulize whereafter the spherulized particles are cooled, characterised in that the feedstock comprises particles of vitreous material which has been subjected to a maximum temperature not exceeding 1400°C in course of its production and in that such feedstock particles are heated to a temperature above 1400°C in the spherulizing furnace.

2. A method of manufacturing vitreous beads, characterised in that vitreous material is withdrawn from a glass-production apparatus at a temperature not exceeding 1400°C, such withdrawn material is formed into solid particles, and such particles are spherulized in a spherulizing furnace in which they are heated to a temperature above 1400°C.

3. A method according to claim 1 or 2, wherein said feedstock particles are particles of incompletely vitrified material including chemically bound substance which evolves as gas on heating in the spherulizing furnace.

4. A method according to claim 3, wherein said feedstock particles include at least 0.25% by weight of said chemically bound substance.

5. A method according to any preceding claim, wherein said feedstock comprises particles of vitreous material which has been subjected to a maximum temperature not exceeding 1370°C in a glass-melting furnace.

6. A method according to any preceding claim, wherein at least a fraction of said particles fed to the spherulizing furnace are in the size range 20μm to 250μm.

7. A method according to any preceding claim, wherein said feedstock is heated to a maximum spherulizing temperature of at least 1500°C in said spherulizing furnace.

8. A method according to any preceding claim, wherein after formation and cooling of the beads they are passed to a settling tank for separating hollow beads from solid beads.

9. A method according to any preceding claim, wherein said feedstock particles are composed of soda-lime glass.

10. A method according to any of claims 1 to 8, wherein said feedstock particles are composed of alumino-silicate, alumino-boro-silicate or boro-silicate glass.

11. Vitreous particles suitable for conversion to glass beads in a spherulizing furnace, characterised in that said particles are composed of vitreous material which has been subjected to a maximum temperature not exceeding 1400°C in course of its formation and at least a fraction of such particles are in the size range 20μm to 250μm.

12. Vitreous particles suitable for conversion to glass beads in a spherulizing furnace, characterised in that said particles are particles of incompletely vitrified material which incorporates at least 0.25% by weight of chemically bound substance which can be converted to gas by heating the particles in a spherulizing furnace to bring about their spherulization.

13. Vitreous particles according to claim 12, wherein said particles or at least a fraction of them are in the size range 20μm to 250μm.

14. Vitreous particles according to any of claims 11 to 13, said particles being particles of incompletely vitrified material wherein a substance which evolves gas on heating to a temperature in excess of 700°C is chemically bound in a unvitrified phase.

15. Vitreous particles according to any of claims 11 to 14, wherein the vitreous material includes chemically bound gas-evolving substance in an amount such that at least 0.25% by weight of the particles can be evolved as gas by heating the particles to a temperature of 1550°C.

16. Vitreous particles according to any of claims 11 to 15, said particles being composed of vitreous material which has been subjected to a maximum temperature not exceeding 1370°C in course of its production.

17. Vitreous particles according to any of claims 11 to 16, such particles being particles of soda-lime glass.

18. Vitreous particles according to any of claims 11 to 16, such particles being particles of alumino-silicate, alumino-boro-silicate or boro-silicate glass.

19. A method of manufacturing vitreous particles which are spherulizable to form vitreous beads on heating in a spherulizing furnace, which method comprises feeding a vitrifiable batch of appropriate composition to a glass-melting furnace, drawing off melt from the furnace before it has been subjected to a maximum temperature exceeding 1400°C, and solidifying the withdrawn melt and reducing it to particle form.

20. A method according to claim 19, wherein the composition of the batch and the furnace conditions to which the melt is subjected before withdrawal are such that the resulting particles are particles of incompletely vitrified material wherein a substance which evolves gas on heating to a temperature in excess of 700°C in a furnace is chemically bound in an unvitrified phase.

21. A method according to claim 19 or 20, wherein the composition of the batch and the furnace conditions to which the melt is subjected before withdrawal are such that the resulting particles include at least 0.25% by weight of a chemically bound substance which can be evolved as gas by heating the particles to a temperature of 1550°C.

22. A method according to any of claims 19 to 21, wherein the maximum temperature to which the drawn off melt has been subjected in the glass-melting furnace is not greater than 1370°C.

23. A method according to any of claims 19 to 22, wherein the solidified melt is reduced to particles at least a fraction of which are in the size range 20μm to 250μm.

24. A method according to any of claims 19 to 23, wherein said melt is drawn off from the melting zone of the glass-melting furnace.

25. A method according to any of claims 19 to 24, wherein said glass-melting furnace comprises a throat leading between melting and refining ends of the furnace and said melt is drawn off from said throat.

26. A method according according to any of claims 19 to 25, wherein said melt is allowed to flow through an opening in the sole of the glass-melting furnace whereafter the exiting flow of melt is drenched with water to solidify the melt and shatter it.

27. A method according to any of claims 19 to 26, wherein said vitrifiable batch has a composition for forming ordinary soda-lime glass.

28. A method according to any of claims 19 to 26, wherein said vitrifiable batch has a composition for forming alumino-silicate glass, boro-silicate glass or alumino-boro-silicate glass.

29. A method according to any of claims 19 to 28, wherein the melt which is solidified and reduced to particle form is drawn off from different regions of the glass-melting furnace.

CLAIMS

Amendments to the claims have been filed, and have the followng effect:–

New or textually amended claims have been filed as follows:–

30. A method according to any of claims 1 to 10, wherein said feedstock comprises particles of incompletely refined or vitrified glass.

31. A method of manufacturing vitreous beads in which a feedstock comprising vitreous particles is fed into a furnace (hereafter called "spherulizing furnace") in which the particles are heated to cause them to spherulize whereafter the spherulized particles are cooled, characterised in that the feedstock comprises particles of incompletely refined or vitrified glass and in that such particles are heated in the spherulizing furnace to a temperature such that they become further refined or vitrified.

32. A method according to any of claims 19 to 29, wherein the melt which is drawn off,

solidified and reduced to particle form comprises incompletely refined or vitrified glass.

33. A method of manufacturing vitreous particles which are spherulizable to form vitreous beads on heating in a spherulizing furnace, which method comprises feeding a vitrifiable batch of appropriate composition to a glass-melting furnace, drawing off unrefined or incompletely refined molten glass from the furnace, and solidifying the withdrawn incompletely refined or vitrified glass and reducing it to particle form.

34. A method according to any of claims 30 to 33, wherein said incompletely refined or vitrified glass includes by weight at least 0.2% undissolved silica.

35. A method according to claim 34, wherein said incompletely refined or vitrified glass includes by weight between 0.2% and 2% undissolved silica.

36. A method according to claim 35, wherein said incompletely refined or vitrified glass includes by weight between 0.2% and 0.5% undissolved silica.

37. A method according to any of claims 30 to 36, wherein said incompletely refined or vitrified glass is drawn off from a glass melting furnace at a location in the melting end thereof.

38. A method according to any of claims 30 to 37, wherein said incompletely refined or vitrified glass is drawn off from a glass melting furnace at a location close to the hot spot thereof.

39. A method according to any of claims 30 to 38, wherein said incompletely refined or vitrified glass is drawn off from a glass melting furnace at a location within the upper or lower one-third of the depth of the melt therein.

40. A method according to claim 39, wherein said incompletely refined or vitrified glass is drawn off from a glass melting furnace through its sole.

41. Vitreous particles manufactured by a method which is according to any of claims 19 to 29, and/or according to claim 32 or 33, and/or according to any of claims 34 to 40 when dependent upon either or both of claims 32 and 33.

42. Vitreous beads manufactured by a method which is according to any of claims 1 to 11, and/or according to claim 30 or 31, and/or according to any of claims 34 to 40 when dependent upon either or both of claims 30 and 31.

43. Vitreous particles according to any of claims 11 to 18, said particles being particles of incompletely refined or vitrified glass.

44. Vitreous particles suitable for conversion to glass beads in a spherulizing furnace, characterised in that said particles are composed of incompletely refined or vitrified glass and in that at least a fraction of such particles are in the size range 20μm to 250μm.

45. Vitreous particles according to claim 43 or 44, wherein said incompletely refined or vitrified glass includes by weight at least 0.2% undissolved silica.

46. Vitreous particles according to any of claims 43 to 45, wherein said incompletely refined or vitrified glass includes by weight between 0.2% and 2% undissolved silica.

47. Vitreous particles according to claim 46, wherein said incompletely refined or vitrified glass includes by weight between 0.2% and 0.5% undissolved silica.

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